

DRAFT SF 298

1. Report Date (dd-mm-yy)		2. Report Type		3. Dates covered (from... to)	
4. Title & subtitle Materials Degradation and Fatigue Under Extreme Conditions Tri-Service Committee on Corrosion Proceedings				5a. Contract or Grant #	
				5b. Program Element #	
6. Author(s) Mr. Lance Ballard, Dr. Jiri Jonas, Dr. Darrell Socie, Dr. Steve Granick, Dr. Andrew Gellman, Dr. K. Jimmy Hsia, Dr. Jian Shang				5c. Project #	
				5d. Task #	
				5e. Work Unit #	
7. Performing Organization Name & Address				8. Performing Organization Report #	
9. Sponsoring/Monitoring Agency Name & Address Tri-Service Committee on Corrosion USAF WRIGHT-PATTERSON Air Force Base, Ohio 45433				10. Monitor Acronym	
				11. Monitor Report #	
12. Distribution/Availability Statement Approved for Public Release Distribution Unlimited					
13. Supplementary Notes					
14. Abstract					
15. Subject Terms Tri-Service Conference on Corrosion					
Security Classification of			19. Limitation of Abstract	20. # of Pages	21. Responsible Person (Name and Telephone #)
16. Report	17. Abstract	18. This Page			

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TRI-SERVICE CONFERENCE ON CORROSION



21-23 JUNE 1994

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Materials Degradation and Fatigue Under Extreme Conditions

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RESEARCH OVERVIEW

This AFOSR University Research Initiative Program (F49620-93-1-0241) addresses complex research problems of materials degradation and fatigue in aerospace structures in severe or extreme environments. A better understanding of materials degradation and flaw initiation dynamics will be achieved through a multidisciplinary research program encompassing chemistry, surface physics, materials science and mechanics, both experimental and theoretical. The main scientific issues are as follows:

- Understanding of stress fields and sources of stress, leading to crack formation;
- Crack nucleation at surface defects;
- Understanding the kinetics and dynamics by which small cracks propagate through solids;

- Perfluoroalkylether surface chemistry, with emphasis on the decomposition reactions of specific functional groups, leading to understanding of fluid degradation and loss of lubricant properties;
- Macroscopic rheological measurements on extreme thin fluid films at extremely high shear rates, leading to understanding of the rheology of lubricant films so thin that continuum understanding does not apply; and,
- NMR and laser Raman scattering measurements of the dynamic structure of highly viscous fluids in contact with solid surfaces in confined geometries at high pressure and temperature.

RESEARCH ACCOMPLISHMENTS

SUB-PROJECT¹: SURFACE CRACK GROWTH UNDER COMBINED MECHANICAL AND HIGH PRESSURE FLUID LOADINGS

The focus of this sub-project has been investigations of the surface crack growth behaviors under combined high hydraulic pressure loading due to lubricants and mechanical loading due to rolling contact. The research work has been pursued with two parallel thrusts. One effort concentrates on the effects of the crack surface friction and the change of frictional stress due to the introduction of lubricants on surface crack growth. The second effort aims at providing a comprehensive solution to the problem involving the interaction between high pressure viscous fluid and a cracked body.

A micromechanics model has been developed to evaluate the effects of crack surface friction on fracture toughness of the materials. The model takes into account the microstructural parameters such as the grain size, grain shape, and frictional coefficient. A self-consistent approach was employed to derive the governing integral equation. The model is capable of predicting the toughening level due to surface friction for infinite and finite sized specimens under externally applied mode III loading. The results demonstrate that even under pure mode III loading, there will be mode I stress intensity at the crack tip induced by the crack surface roughness. The model predictions of mixed mode I/mode III fracture toughness agree very well with existing experimental measurements. Furthermore, the effect of lubricant is studied by changing the frictional coefficient. The result shows that, by introducing lubricant, the toughening is reduced, thus resulting in a higher crack tip stress intensity and a higher crack growth rate.

The effects of high pressure viscous fluid on surface crack growth have been studied by using fluid mechanics and fracture mechanics approaches. We considered a crack filled with a linear viscous fluid in a semi-infinite body and with a large fluid reservoir outside the crack mouth. The pressure history in the fluid reservoir was prescribed. It was found that the governing equations of this problem were two coupled non-linear integral equations of two unknown functions, the pressure distribution inside the crack $p(x,t)$ and the crack face opening displacement $h(x,t)$. To simplify the problem, a local pressure-displacement relation was assumed. Analytical solutions were obtained using separation of variables. The results indicate that there exists a characteristic time which is a function of viscosity of the fluid, Young's modulus of the solid, and the ratio of crack length to the average opening displacement of the crack. If the period of the external loading is much longer than the characteristic time, the pressure distribution in the crack is nearly uniform, resulting in a high crack tip stress intensity. On the other hand, when the period of external loading is much shorter than the characteristic time, pressure will not be transmitted deep into the crack, resulting in a low crack tip stress intensity. This result can be used to guide the experimental part of this project.

SUB-PROJECT²: FLUID-ASSISTED FATIGUE CRACK GROWTH IN CERAMICS

This sub-project is concerned with the role of the lubricant as a corrosive fluid assisting in fatigue crack growth. Under high pressure and high temperatures caused by the heat generated by friction at the contact location, the lubricant could decompose into corrosive fluid. At the crack tip, the interaction between the corrosive fluid and the crack tip is mutual: the chemical reaction (corrosion) will enhance the crack growth rate; on the other hand, the high crack tip stress will accelerate the chemical reaction rate. Thus when exposed to a corrosive environment, the crack growth rate will be faster.

As microcracks grow longer, transition from an initial Mode-II crack (also known as a stage-I crack) to a Mode-I (stage-II) may occur at some crack length. Crack growth is governed by different driving forces before and after the transition and will likely follow different growth laws. The growth laws will be established in terms of the growth rate as a function of stress or stress intensity as appropriate. The growth rate of microcracks will be measured by the surface replicating technique in combination with periodic inspection of crack shapes. The transition crack length will be determined in different microstructural and environmental conditions.

Our investigation thus far on fatigue crack growth in a fluorinated oil (Krytox, DuPont) and air has shown that lubricants can have a significant effect on the fatigue failure of silicon nitride (Si_3N_4). Fluorinated oil, despite its excellent chemical stability, accelerates fatigue crack growth in Yttrium (Y) - containing Si_3N_4 . In particular, the growth rate of surface microcracks in the fluorinated oil was found to be about twice the rate in air. Our preliminary work indicates that the oil assisted fatigue crack growth in Y-containing Si_3N_4 by dissolving Y-containing grain boundary phase, thereby reducing the effectiveness of acicular grains in crack bridging. The effect could be aggravated in real bearing applications where the chemical stability of the oil may be adversely affected by the high pressure and high temperature.

SUB-PROJECT³: SURFACE INDUCED DEGRADATION OF FLUOROCARBON LUBRICANTS

The focus of this sub-project has been a study of the surface chemistry of fluorocarbons, with a particular interest in the understanding of surface chemical reactions important in tribological applications. The relevance of fluorocarbons to tribological applications derives from the extremely high thermal stability of the perfluoroalkylethers (PFAEs) which makes them suitable for use as lubricants under high temperature conditions. Their deficiency arises from the fact that little is known about the types of materials that can be used as boundary layer additives. The materials classically used as boundary layer additives in hydrocarbon lubricant fluids are amphiphilic in nature and serve to coat metal surfaces with thin surfactant-like films. These prevent metal surfaces in sliding contact from actually reaching the point of direct metal-metal contact. These additives both lubricate the surfaces and prevent the wear that would result from direct metal-metal contact. Most of the hydrocarbons that would normally be considered for use as additives in hydrocarbon fluids are neither soluble in the fluorocarbons nor stable to the temperatures at which the fluorocarbons are used.

The fundamental goal of this program is an understanding of surface chemical problems in lubrication and in particular in lubrication by fluorocarbons. Over the past year we have studied a number of reactions of fluorocarbons on metal surfaces in order to deepen our understanding of the role that fluorine plays in influencing surface reaction kinetics. We have focused on the reactions of fluorinated olefins on copper (Cu) surfaces and on the coupling reactions of alkyl groups on silver (Ag) surfaces. While fluorination has little influence on the π -bonding of the olefins to metal surfaces, fluorination of alkyl groups dramatically lowers the rates of coupling. Other work has included

development of measurement techniques for our surface studies. In one case, our ultra-high vacuum (UHV) tribometer has been used to look at friction of Cu(111) surfaces lubricated by submonolayer films of fluorinated ethanol. Most recently we have set up a Fourier Transform Infrared (FTIR) spectrometer for measurements of vibrational spectra of adsorbed monolayers on metal surfaces in ultra-high vacuum. This has been used to obtain spectra of a series of fluorinated ethoxides on the Cu(111) surface. These are to be used to begin determining the orientations of adsorbed species used as lubricants.

SUB-PROJECT⁴: FLUIDS, INCLUDING LUBRICANTS, UNDER EXTREME CONDITIONS OF HIGH PRESSURE, HIGH TEMPERATURE, AND CONFINEMENT

This sub-project deals with nuclear magnetic resonance (NMR) and laser Raman scattering experiments on highly viscous liquids, including lubricants, both in bulk and in confined geometries, over a wide range of pressures and temperatures. In a general sense, we focus on the relationship between molecular level properties as obtained from our experiments and the macroscopic properties of the fluids studied, including fluids at the fluid-solid interface. This focus allows molecular correlations with rheological properties such as viscosity.

In continuation of our systematic efforts to improve the understanding of the dynamic behavior of confined fluids, we have carried out NMR relaxation experiments on a number of molecular fluids, including model lubricants. Our studies of confinement effects on relaxation of polar and nonpolar molecules have confirmed a two-dimensional theoretical explanation. Application of a two-state, fast exchange model allows separation of surface effects from bulk liquid effects, which in turn provides insight into the dynamic behavior and viscosity of the surface layer. Recent applications of the two-state, fast exchange model to additional model systems provide us with a stronger basis for actual lubricant studies in the near future.

A very important aspect of our research is the further development of unique NMR and other instrumentation to permit studies of various materials under extreme conditions of pressure and temperature. This includes our recent development of NMR probes and pressure generating systems which permit measurements up to pressures of 10kbars. Our long-term goal to improve our expertise in the experimental techniques for extreme conditions is not only of basic research importance, but it also has direct technological relevance to the Air Force mission.

This relevance is reflected in our work with the model lubricant ethylhexylbenzoate (EHB), including an earlier bulk liquid study to 5kbars and our recent confinement studies. The bulk liquid study has provided the framework for current work with the closely related lubricant, di-(2-ethylhexyl)phthalate (DEHP). These studies should help to separate the effects of structure on the motional dynamics of lubricants. Our confinement studies of EHB have shown the applicability of the two-state, fast exchange model to a model lubricant system, as well as the domination of geometric confinement effects over surface interaction effects at low frequency. We are currently in the process of extending these confinement studies to model fluorinated lubricants. These studies will be supplemented by studying pressure effects on confined liquids using our unique techniques.

SUB-PROJECT⁵: MOLECULAR TRIBOLOGY OF PERFLUOROETHER LUBRICANTS

This sub-project revolves around the tribology of perfluoroether fluids under extreme, but nonetheless well-defined, conditions of shear rate and confinement. The experimental design consists of an idealized single asperity: fluid films sandwiched between atomically smooth solid surfaces that are close together at a controlled separation (5-500 Angstroms) but not actually touching. The film thickness and shear displacements can be controlled to 1 Å, at shear rates from 10^{-2} to 10^5 sec^{-1} . A unique feature is the capacity to measure not only conventional dissipative friction, but also fluid elasticity.

The friction behavior of model lubricants, either fluorinated or hydrogenated, has been compared. In both cases, the liquids were confined between two atomically smooth parallel mica plates. The method of measurement was a surface forces apparatus, modified for oscillatory shear. Some observations were the same in both cases: (1) Predominantly elastic behavior in the linear response state was followed by a transition to a mostly dissipative state at larger deformations. The elastic energy stored at the transition was low, of the order of 0.1 kT per molecule. This transition was exactly repeatable in repetitive cycles of oscillation and reversible. (2) The dissipative stress in the sliding state was only little dependent on peak sliding velocity when this was changed over several decades. Significant (although smaller) elastic stress also persisted, which decreased with increasing deflection amplitude. (3) The transition back to the solid-like state appears to be more gradual than in the opposite direction, probably indicating different processes.

Two major differences between fluorinated and hydrogenated systems were observed: (1) For fluorinated molecules, the shear stress in the sliding regime was mostly higher than in the solid-like state, whereas for hydrogenated molecules this stress was significantly lower. (2) Fluorinated molecules needed long relaxation times (several minutes) to adjust to changes in the applied stress.

In the above experiments, the mica surfaces were not damaged, as was confirmed by the reproducibility of the results. However, at large amplitudes and high frequencies of oscillation, damage was observed giving rise to characteristic changes in the responding stresses, as well as the thickness of the lubricant film.

ACKNOWLEDGEMENT

This work was supported in part by the Air Force Office for Scientific Research (FOSR) under Grant F49620-93-1-0241 and by the Augmentation Awards for Science and Engineering Research Training (AASERT) Program under Grant F49620-93-1-0555.

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